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Bis(tributyltin) oxide as a wood preservative: its chemical nature in timber

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Tributyltin compounds have been used for many years as wood preservatives. This study has provided, for the first time, an explanation for the previously reported dealkylation and/or volatilization of the tributyltin species in, and from, timber. Thus ^{119}Sn NMR studies have shown that, on impregnation into timber, bis(tributyltin) oxide, $(Bu_3Sn)_2O$, is rapidly converted to other tributyltin species, Bu_3SnOX, and that these subsequently undergo disproportionation to Bu_4Sn and $Bu_2Sn(OX)_2$ compounds. We have additionally demonstrated that Bu_4Sn, so produced, is not persistent in timber and is lost by volatilization. Since the rate of disproportionation of the Bu_3SnOX species should be dependent upon the nature of the X group, it should be possible to affect significantly, if not to stop, this process by the use of alternative tributyltin fungicides, e.g. tributyltin methanesulphonate. However, tributyltin fungicides have been used successfully in wood preservation for at least 25 years. Therefore, it must be concluded that, even after disproportionation in timber, in service, sufficient preservative action is retained to prevent decay of wood under the conditions of natural exposure.

Keywords: Bis(tributyltin)oxide, wood preservation, degradation, timber

INTRODUCTION

In recent years, tributyltin compounds, in particular bis(tributyltin) oxide, $(Bu_3Sn)_2O$, have found extensive use as fungicides in organic-solvent-based wood preservatives.[1,2] It has been reported, however, that the triorganotin compound undergoes dealkylation in timber to less biologically active species.[3] Furthermore, it has been observed that the total tin content of the timber decreases with time.[4] Despite these reports, reports of failure of double-vacuum-treated joinery timber are remarkably scarce. To date, neither the chemical nature of the organotin compound, nor the mechanism by which it protects the substrate against decay, is well understood. A knowledge of these processes will enable the development of more efficient, stable and environmentally acceptable preservatives, with a wider range of applications.

Herein, we report analytical data for the organotin species present in *Pinus sylvestris* treated with $(Bu_3Sn)_2O$, together with ^{119}Sn NMR spectroscopic data of benzene extracts from this wood substrate. The results are interpreted and discussed in terms of a dealkylation pathway for the organotin preservative.

EXPERIMENTAL

Bis(tributyltin) oxide, $(Bu_3Sn)_2O$, was obtained from Schering AG, West Germany, and was used without further purification. Tetrabutyltin, Bu_4Sn, was prepared according to a previously published procedure.[5]

Treatment of wood blocks

(a) For the quantitative analytical study of the organotin species present in timber, blocks of *P. sylvestris* sapwood (30 mm × 10 mm × 5 mm) were first dried at 105°C for 18 h. The blocks were allowed to cool in a desiccator for 30 min and were then vacuum-impregnated with a petroleum ether (b.p. 60–80°C) solution of $(Bu_3Sn)_2O$ (0.2% w/w) as described previously.[6] After standing for 2 h, surface liquid was removed by blotting and the blocks were cut into three equal portions and allowed to dry for three weeks at ambient temperature in open Petri dishes. Analytical investigation, using Methods 1 and 2 below, was then performed and repeated after a further 4 and 14 weeks of standing on glass plates, either in the laboratory or in an oven at 60°C.

(b) For the NMR investigation of the organotin species present in timber, 30 blocks of *P. sylvestris* sapwood

(30 mm × 10 mm × 5 mm) were treated with a solution (2.0% w/w) of $(Bu_3Sn)_2O$ in petroleum ether (b.p. 60–80°C) in the manner described above but without prior drying. After 24 h, 10 blocks were Soxhlet-extracted for 48 h in 200 cm^3 benzene. The resultant solution was concentrated to approximately 10 cm^3 prior to NMR investigation. The remaining blocks were stored in sealed 250 cm^3 conical flasks (2 × 10 blocks) and allowed to stand in the laboratory at ambient temperature or in an oven at 60°C for 12 weeks, after which they were Soxhlet-extracted with benzene as before and NMR investigation again performed. This overall procedure was repeated four times in order to check the consistency of results.

(c) A study of the persistence of Bu_4Sn in timber was performed by treating 10 blocks of *P. sylvestris* sapwood (30 mm × 10 mm × 5 mm) with Bu_4Sn in the manner described in (b). 5 blocks were analyzed for their total tin content (Method 1) after 24 h. The remainder were allowed to stand on glass plates in the laboratory for 2 weeks prior to analysis.

Analytical procedures

Method 1. Determination of the total tin content of wood blocks

The blocks were initially weighed and then wet-ashed with sulphuric acid/nitric acid and the samples diluted with water to produce a 10% v/v sulphuric acid solution. The tin content of the resultant solutions was then determined by flame atomic absorption spectrophotometry.

Method 2. Determination of the organo-/inorganic tin species in the wood blocks

The blocks were macerated in a blender and part of the sample subjected to total tin analysis as described in Method 1. The remainder was subjected to Soxhlet extraction, for 2 h, in dichloromethane. The organo-/inorganic tin species in the resultant solution were determined by paper chromatographic separation, followed by determination of the tin content using a graphite furnace atomic absorption spectrophotometer as described previously.[7] The residual tin in the timber was calculated by difference. The extracted wood blocks were then further refluxed with methanol containing 0.5% hydrochloric acid for 10 min and the tin species present again determined.

Method 3. Determination of the butyltin species present in benzene extracts obtained from wood block treatment procedure (b)

Concentrated extraction solution (10–20 μL) was placed on a TLC plate and the species separated using cyclohexane/acetic acid/acetone (31/1/6 parts by volume). Spots were developed by spraying the plate with a catechol violet solution and exposing to UV light.[8] R_F values obtained by this system are as follows: $SnY_4/BuSnY_3$, 0.0; Bu_2SnY_2, 0.55; Bu_3SnY, 0.85; Bu_4Sn, 0.95. (N.B. The nature of Y does not affect the R_F value provided it is an anionic moiety.)

^{119}Sn NMR spectroscopy

^{119}Sn NMR spectra were recorded on a JEOL FX6OQ at 22.24 MHz, under nuclear Overhauser suppressed conditions. Field frequency lock was to external D_2O. ^{119}Sn chemical shifts are relative to Me_4Sn and are accurate to ±0.5 ppm.

RESULTS AND DISCUSSION

Table 1 presents the results of a quantitative speciation of the tin content in *Pinus sylvestris* wood blocks treated with $(Bu_3Sn)_2O$, after storage on glass plates in the laboratory or in an oven at 60°C for 14 weeks. The results obtained from the 60°C blocks indicated that a considerable amount of unextractable (by dichloromethane) or residual tin remained in the timber. This was removed by a further reflux with methanol containing 0.5% hydrochloric acid, and was found, after speciation, to consist essentially of di- or mono-/inorganic tin species. The extent of residual tin that cannot be extracted by dichloromethane has been previously discussed.[7,9] It is apparent from Table 1 that substantial dealkylation of the tributyltin fungicide occurs within a relatively short period of time. In addition, it is seen that breakdown occurs more rapidly at the higher temperature. A temperature of 60°C, employed for these studies, is not unrealistic, since window joinery painted with dark paints can reach a temperature of 70°C on the surface and 50°C at a depth of 5 mm on a hot summer day.[10] It must be mentioned, however, that owing to the small sample size studied, more generalized rates of degradation should not be inferred from the data in Table 1, since variation will arise due to the variety and inhomogeneity of timber.[11]

In order to gain more insight into the mechanism(s)

Table 1 Speciation data of $(Bu_3Sn)_2O$-treated *Pinus sylvestris* blocks[a]

Time (weeks)[b]	Temp (°C)	Total Sn in block (% w/w)[c]	Bu_3SnY (% as Sn)[d]	Bu_2SnY_2 (% as Sn)[d]	$BuSnY_3/SnY_4$ (% as Sn)[d,e]	Residual Sn (% as Sn)[d,f]
0	—	0.08	85	10	—	5
0	—	0.05	90	—	—	10
4	25	0.06	75	15	—	10
4	25	0.06	75	15	—	10
14	25	0.06	75	10	—	15
4	60	0.06	50	25	—	25
			50[g]	40[g]	10[g]	—[g]
14	60	0.05	10	40	5	45
			10[g]	60[g]	25[g]	5[g]

[a] Obtained from analysis of CH_2Cl_2 extracts. [b] Measured after a 3-week drying period. [c] Error = ±0.01%. [d] Error = ±5%. [e] The chromatographic procedure employed does not separate $BuSnY_3$ and SnY_4 derivatives. [f] See text. [g] After additional extraction — see text.

of dealkylation of the tributyltin preservative, Soxhlet extractions of *Pinus sylvestris* blocks treated with $(Bu_3Sn)_2O$ were studied by ^{119}Sn NMR. Analytical results of blocks treated according to method (2) revealed that the average loading of tin in each block was initially 1% w/w [i.e. approx. 2.5% $(Bu_3Sn)_2O$]. ^{119}Sn NMR spectra of benzene extracts from freshly treated blocks, i.e. extracted within 24 h of treatment, showed in each case a broad asymmetric peak (linewidth approx. 60 Hz) centred at approximately 91 ppm, together with minor resonances at approximately 84, 99 and 106 ppm. (A typical spectrum is shown in Fig. 1B.)

These spectra should be compared to that of $(Bu_3Sn)_2O$ in benzene (200 mg cm^{-3}), which has a single resonance (linewidth approximately 7 Hz) at 84.1 ppm (Fig. 1A). Consequently, although some evidence of $(Bu_3Sn)_2O$, at 84 ppm, is seen in the spectra of the extract solutions it is apparent that treatment of the wood blocks with this organotin results in an immediate change in the nature of most of the organotin. A similar change has been reported elsewhere.[12] Spectra of extracts from blocks stored in sealed conical flasks at room temperature were essentially unchanged from those of the freshly treated and extracted blocks. However, spectra resulting from samples stored at 60°C in sealed conical flasks showed three main resonances at *ca* 91, -11.4 and *ca* -152 ppm (a typical spectrum is shown in Fig. 1C). Although these three features were consistently observed, the relative intensity of each was seen to vary. For example, integration of the ^{119}Sn NMR spectra showed that the peak at -11.4 ppm accounted for between 5 and 15% of the total tin content of the solution. The peak at *ca* 91 ppm is presumably due to the same species as was present in the extracts from the freshly treated blocks, and the chemical shift value is typical of a Bu_3SnOX derivative. Such a compound would not be unexpected when the constituents of wood e.g. cellulose, lignin, carboxylic acids, etc. are considered, each of which contain C—OH groups, of which the H is replaceable by Bu_3Sn.[5]

Further work is under way to establish the nature of X on the tributyltin moiety. The peak at -11.4 ppm in the ^{119}Sn NMR spectra is ascribed to Bu_4Sn [δ ^{119}Sn(neat Bu_4Sn) = -11.7 ppm]. The third feature (δ ^{119}Sn = *ca* -152 ppm) in the ^{119}Sn NMR spectra of the extracts from blocks stored at 60°C is representative of certain $Bu_2Sn(OX)_2$ derivatives, which are known[5] to exist in a dimeric form in which the tin atom is five-coordinate. Again, further work will be required to establish the nature of the X group. In order to verify the presence of the different butyltin species in the extract solutions, as indicated by ^{119}Sn NMR, qualitative TLC analysis was performed. This clearly confirmed the presence of Bu_4Sn, Bu_3SnY and Bu_2SnY_2 in the solution obtained from the blocks stored at 60°C. A similar investigation on extracts obtained from either freshly treated blocks or those stored at room temperature showed essentially just Bu_3SnY derivatives.

This study has therefore demonstrated, we believe for the first time, that Bu_4Sn is produced in timber which has been treated with $(Bu_3Sn)_2O$. The formation of this species, together with the associated dibutyltin derivatives, may be explained by a disproportionation reaction, i.e.

$$(Bu_3Sn)_2O \xrightarrow{\text{timber}} 2Bu_3SnOX \longrightarrow Bu_4Sn + Bu_2Sn(OX)_2$$

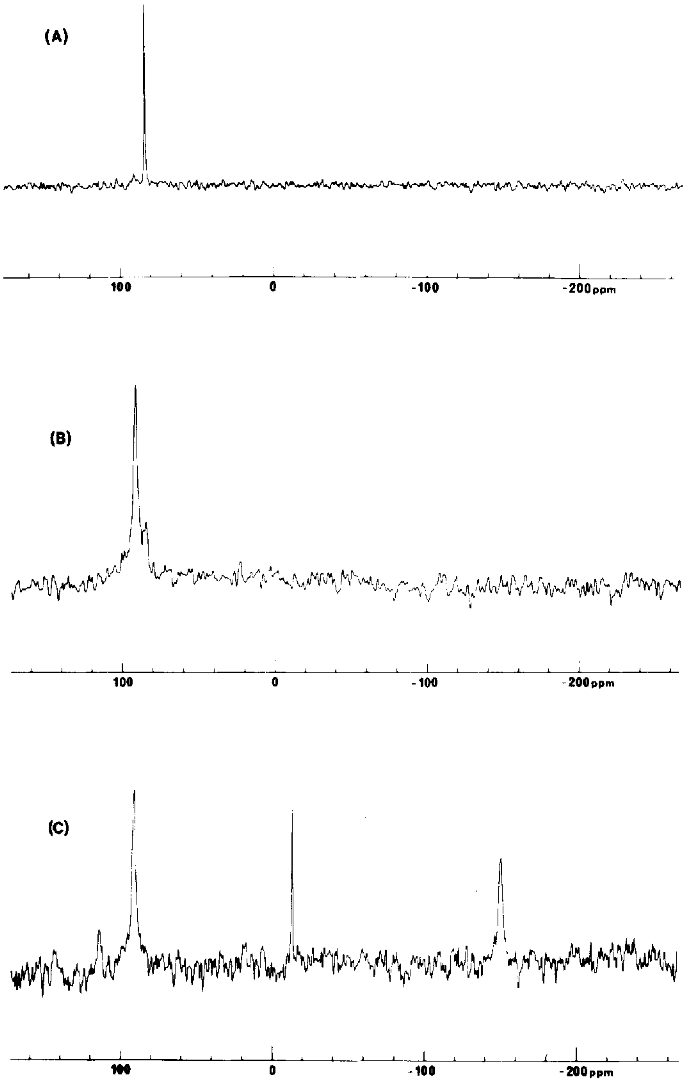

Figure 1 ^{119}Sn NMR spectra of (A) $(Bu_3Sn)_2O$ in benzene (200 mg cm^{-3}); (B) a benzene extract solution of $(Bu_3Sn)_2O$-treated *Pinus sylvestris* sapwood blocks, obtained 24 h after treatment; (C) a benzene extract solution of $(Bu_3Sn)_2O$-treated *Pinus sylvestris* sapwood blocks which had been stored at 60°C for 12 weeks.

Such a reaction has precedence from previous studies of certain Bu_3SnOX derivatives.[13,14] Obviously, the rate of disproportionation will be dependent upon the nature of the X group in the Bu_3SnOX compound. It should therefore be possible to affect significantly, if not to stop, this process by the use of alternative tributyltin fungicides, e.g. tributyltin methanesulphonate (Bu_3SnOSO_2Me), which are less reactive and so are unlikely to form the same Bu_3SnOX species in timber.

From Table 1 it may be seen that monobutyl-/inorganic tin compounds were determined as being present in wood blocks treated with $(Bu_3Sn)_2O$, particularly those stored at 60°C. The above disproportionation reaction does not account for the formation of such species. It must therefore be inferred that other dealkylation pathways are occurring simultaneously.[3,15] These monobutyl-/inorganic tin derivatives were not detected in the NMR study of the extract solutions and indeed TLC analysis suggested only trace quantities. However, as mentioned previously and shown in Table 1, an additional extraction is required to remove such compounds from timber. In fact, analysis of one set of blocks which had been stored at 60°C and Soxhlet-extracted with benzene revealed an average tin content of 2.3 mg Sn/g timber, i.e. only approximately 50% of the total tin content had been removed. Thus, it is likely that such $BuSnY_3/SnY_4$ species were present in the blocks but were not extracted.

Previous studies have reported[4] the apparent loss of organotin preservative from timber with respect to time. The formation of Bu_4Sn could also explain this phenomenon, since it was demonstrated that *Pinus sylvestris* blocks, treated with Bu_4Sn (average initial loading = 1.6% w/w) showed on average a 70% loss of organotin after standing on glass plates in the laboratory for two weeks at ambient temperature. For this reason the non-observaton of Bu_4Sn in the results shown in Table 1 can be explained, since the blocks were not kept in sealed containers and so any Bu_4Sn produced would presumably have volatilized. In fact, volatilization may explain the non-observation of Bu_4Sn in the previous works.[3,4]

It has been observed that there have been relatively few failures of $(Bu_3Sn)_2O$-treated timbers in service life. This is perhaps at first surprising when one considers the results presented herein, i.e. that the initial tributyltin biocide is changed to other butyltin products. It is known that the toxicity values to fungi of all tributyltin compounds are similar. Hence the initial reaction of $(Bu_3Sn)_2O$ to form Bu_3SnOX will not significantly affect the biocidal efficacy. Although it is generally accepted that the fungicidal activity of dibutyltin compounds is less than that of tributyltin derivatives, it is important to remember that they do still possess significant biological activity. In fact, there have been very few reports[4,16] of laboratory wood block tests, designed to assess the comparative activity of analagous di- and tri-organotin compounds. Furthermore, there are other factors to be considered in the role of a wood preservative formulation, e.g. prevention of the ingress of water, and it is known that certain organotin compounds are effective water repellents.[17,18] In addition, laboratory evaluations of preservative effectiveness are necessarily accelerated and, therefore, provide conditions that are much more severe than are encountered in natural conditions. Thus, although dealkylation of the triorganotin preservative occurs in timber to produce tri-, di- and mono-butyltin mixtures, sufficient preservative action is retained to prevent decay under the conditions of natural exposure.

CONCLUSIONS

It has been shown that $(Bu_3Sn)_2O$ undergoes rapid conversion in timber to form other tributyltin–oxygen species, Bu_3SnOX. A pathway for the known dealkylation of tributyltin compounds in wood has been identified as the disproportionation of the Bu_3SnOX derivatives, leading to the formation of Bu_4Sn and $Bu_2Sn(OX)_2$ compounds. The Bu_4Sn produced is lost from the timber by volatilization. Since the rate of disproportionation should be dependent upon the nature of the X group it should be possible to affect significantly, if not to stop, this process by the use of alternative tributyltin fungicides, e.g. tributyltin methanesulphonate. Nevertheless, other dealkylation pathways will exist in timber, resulting in mixtures of tri-, di- and mono-butyltin species. However, tributyltin fungicides have been used successfully in wood preservation for at least 25 years. Therefore, it must be concluded that the resultant mixture retains sufficient preservative action to prevent decay of timber under the conditions of natural exposure.

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